PATENT ABSTRACTS OF JAPAN

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(54) OPTICAL INFORMATION MEDIUM

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain an optical information recording medium having high performance and excellent in aging stability by forming a metallic reflecting layer with an Ag alloy obtained by incorporating a specified amount of Cu into Ag and then disposing a sulfur-free organic or inorganic protective layer or an adhesive layer on the metallic reflecting layer.
SOLUTION: The optical information medium, which is not a magneto-optical recording medium, has a metallic reflecting layer comprising an Ag alloy obtained by incorporating 0.5-30 at.% Cu into Ag and has an organic or inorganic protective layer not substantially containing elemental sulfur or an adhesive layer on the metallic reflecting layer. When the reflecting layer comprises an Ag alloy obtained by incorporating 0.5-30 at.% Cu and 0.5-12 at.% at least one of Ta and Ti into Ag, considerably enhanced recording sensitivity and corrosion resistance are ensured. The metallic reflecting layer is preferably applied to a phase change type optical recording medium.

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CLAIMS

[Claim(s)]
[Claim 1] The optical information media characterized by forming the protective layer or glue line which a metallic reflective layer is set to Ag from Ag alloy which does 0.5-30 atom % content of Cu in the optical information media except the magneto-optic-recording medium which has a metallic reflective layer, and does not contain S (sulfur) element substantially on a metallic reflective layer.
[Claim 2] The optical information media according to claim 1 to which Ag does [a metallic reflective layer] 0.5-30 atom % content of Cu, and it is further characterized by the bird clapper from Ag alloy of Ta or Ti which does 0.5-12 atom % content of a kind at least.
[Claim 3] The optical information media according to claim 2 characterized by an optical information media being a phase-change type optical recording medium.
[Claim 4] An optical information media given in either of the patent claims 1-3 characterized by being the film surface incidence type which has the structure with which the optical information media formed at least one record layer on the substrate, and performs read-out (reproduction) of the information by the laser beam, and/or informational writing (record) from a record layer side, without letting a substrate pass.
[Claim 5] The optical information media according to claim 3 to 4 which the record layer of an optical information media makes germanium, Sb, and Te a principal component, and is characterized by thickness being 10-40nm.

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* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] By light, such as laser, this invention relates to the optical information media which performs informational reproduction, record, elimination, etc. and which has a metallic reflective layer. It is related with the phase-change type optical recording medium which uses for informational record and elimination the reversible structural change between the amorphous state of the matter produced by irradiation of a condensing laser beam, and a crystallized state (phase change) still in detail especially about a disk-like medium. Furthermore, it is related with the optical information media of the film surface incidence type with which research and development are progressing in recent years.
[0002]
[Description of the Prior Art] Various optical information medias (optical disk) are used. As a type only for reproduction, CD (compact disk) and a CD-ROM disk are famous, there is a CD-R disk as a type which can be written in only at once, and there are a magneto-optic-recording disk and a phase-change record disk as a record / eliminable type. As a phase-change disk, the CD-RW disk, PD disk, and the DVD-RAM disk are marketed. It is the most important medium as a mass animation record medium for which a phase-change type optical recording medium attracts attention as mass rewriting types, such as DVD-RW, especially in recent years and which replaces future videotape.
[0003] The phase-change type optical recording medium uses for informational record and elimination the reversible structural change (phase change) between the amorphous state of the record layer in which induction is carried out by the difference in the heat history of the temperature up and cooling by optical irradiation (laser beam irradiation), and a crystallized state. Namely, it eliminates by carrying out heating fusion and quenching a record layer by making it crystallize by recording by making it un-crystallize, and carrying out fixed time maintenance more than crystallization temperature. The temperature of a record layer (typical GeSbTe film) is presumed to become about 600 degrees C at the time of record, and to become about 170 degrees C at the time of elimination. Reproduction of a signal is performed using the reflection factor difference between an amorphous state and a crystallized state. In addition to an informational high-speed throughput, such a phase-change type optical recording medium has large storage capacity. Moreover, the merit made at a low price than it is easier than a magneto-optic-recording drive also has the structure of drives (optical head etc.). By this phase-change type optical recording medium, usually, the crystallized state of record film is made into an informational elimination state, and the amorphous state (amorphous mark) generated by melting of the film by the high laser power and quenching is made into a record state.
[0004] Electronic-intelligence communication society The structure of the typical phase-change disk currently used for present is shown in the technical research report [electronic parts and material] CPM 90-35 and pp 43-48 "the quenching tectofacies change light information media using ZnS-SiO2 dielectric" (July 27, 1990). the structure -- a polycarbonate substrate (it is usually the thickness of 0.6mm or 1.2mm) / a lower dielectric layer (ZnS-SiO2 film) / record layer (GeSbTe film) / up dielectric

layer (ZnS-SiO2 film) / reflecting layer (aluminum alloy) / glue line -- it comes out
[0005] Moreover, by the film surface incidence type medium by which research was started, the usual idea makes reverse built-up sequence of the thin film from a substrate to the usual medium of marketing of these present. That is, it inquires with the composition of a substrate / reflective film / lower dielectric / record film / up dielectric. The same structure as a hard disk is proposed according to the need that the optical head (pickup) used makes an objective lens approach a medium side. That is, use of the surfacing head which carried the objective lens in the slider is considered.
[0006] As for the record layer of a phase-change type optical recording medium, chalcogen alloys, such as GeSbTe and AgInSbTe, are used so that the aforementioned reference may see. The film of ZnS systems, such as ZnS-SiO2, is used for a dielectric film. As for the reflecting layer, aluminum alloy film, Au film, Ag film, etc. are used. With aluminum alloy, the AlTi film and AlCr film containing several% of Ti or Cr are used abundantly. By the media (CD-R disk etc.) which use an organic coloring matter as a record layer, Au film and Ag film are used as a reflecting layer. Generally in CD only for reproduction (compact disk), aluminum film is used.
[0007]
[Problem(s) to be Solved by the Invention] aluminum alloy film with which the above is used, Au film, and Ag film have the following technical problems. Although aluminum alloy film is produced by the spatter using the target which consists of this alloy, since the melting point must build this alloy target with the alloy of two kinds of greatly different metals, it is not easy to manufacture, and according to the spatter yield of aluminum being bad, the film rate of sedimentation of sputtering is slow, and it has a fault, like (the reflection factor of a film simple substance) has a reflection factor comparatively as low as 80 - 85%. Although Ag film has about 100% of reflection factor, it has the fault that a corrosion resistance is not good. Although Au film is stable, it is very expensive. That is, the present condition is that search of the reflecting layer which carries out simultaneous satisfaction of all, such as a performance, a price, and production speed, is continued.
[0008] This invention persons proposed the reflecting layer of an AgCuTi alloy and an AgCuTa alloy before. Although the alloy film in that case was applied to the magneto-optic-recording medium and achieved fixed success, it has a technical-problem **** case in the application of those other than a magneto-optic-recording medium, and sufficient result was not obtained. Especially, by the phase-change type optical recording medium, the technical problem that Ag would sulfurate and a reflection factor would fall on the reflecting layer of Ag system alloy if spatter film production of this dielectric film is carried out occurred from using ZnS-SiO2 film as a dielectric layer.
[0009] It was made in view of this present condition, and a reflection factor is high and this invention excels [reflection factor] in corrosion resistance, and it is specifying the good reflecting layer of productivity, and the protective layer on it, and it aims at offering a highly efficient and cheap optical information media, especially a phase-change type optical recording medium.
[0010]
[Means for Solving the Problem] This invention persons found out that the optical information media which formed the metallic reflective layer with the AgCu alloy, and was cheap with high performance by preparing organic or inorganic the protective layer or glue line which does not contain S (sulfur) on this metallic reflective layer, was excellent in productivity, and was further excellent in stability with the passage of time was obtained, as a result of considering wholeheartedly improvement of the metallic reflective layer which carries out simultaneous satisfaction of all, such as a performance, a price, and production speed, like the above.
[0011] That is, in the optical information media except the magneto-optic-recording medium by which this invention has a metallic reflective layer, this metallic reflective layer is the optical information media characterized by forming organic or inorganic the protective layer or glue line which consists of an Ag alloy to carry out, and does not contain S element substantially on this metallic reflective layer 0.5-30 atom % content about Cu (copper) at Ag (silver). Furthermore, this invention is an optical information media which carries out and makes a reflecting layer further Ag alloy of Ta (tantalum) or Ti (titanium) which does 0.5-12 atom % content of a kind at least 0.5-30 atom % content about Cu at Ag.

Moreover, the metallic reflective layer of this invention is preferably applied to a phase-change type optical recording medium.

[0012]

[Embodiments of the Invention] Although this invention persons paid their attention to Ag film of a high reflection factor for the purpose of the improvement in a regenerative-signal noise ratio (C/N), Ag is a corrosion resistance bad material and they are not practical only by Ag film. Then, when addition of other metals was considered as this improvement, the AgCu alloy film which did 0.5-30 atom % addition of Cu formed on slide glass was a high reflection factor, even if it left it for 72 hours or more under the 80-degree-C85% relative humidity atmosphere which is the standard acceleration degradation test condition of an optical information media, a reflection factor did not fall, but a certain thing also made endurance clear. In addition, even if there were few contents of Cu than 0.5 atom %, the reflection factor fell to 90 or less percent of initial value within at most 24 hours from 30 atom %. The AgCu alloy film was as above-mentioned a quantity reflection factor (for example, with an Ag85Cu15 (subscript is atomic % composition) alloy film, it is 98% of reflection factor at the wavelength of 780nm), and since endurance was not bad, either, it made it clear that it is suitable for the optical information media only for reproduction. However, this AgCu film had high thermal conductivity, therefore it became clear further that record sensitivity falls by the phase-change type optical recording medium which makes this a reflective film.

[0013] Further, paying attention to improvement of this point, wholeheartedly, this invention persons found out the thing of Ta or Ti which record sensitivity and corrosion resistance improve greatly to addition of the 3rd element at the AgCu film as a result of research, when 0.5-12 atom % addition of a kind was done at least. In addition, when there are few contents of Ta and Ti than this range, there is no effect of improvement in record sensitivity, and if it increases conversely, reflection will fall and C/N will become bad. Furthermore, 1.5 - 10 atom % is more desirable at the point that the content of Ta and Ti has the large improvement effect in sensitivity, and the effect of the improvement in C/N is not checked by the phase-change type optical recording medium. In addition, in order to improve stability with the passage of time further, you may carry out little addition of other elements, such as Cr, Nb, and Re.

[0014] The thickness of this metallic reflective layer is used preferably 3-200nm. When considering absorption coefficient amendment composition which makes the rate of an optical absorption in case a record layer is a crystallized state larger than the rate of an optical absorption at the time of an amorphous state by the phase-change type optical recording medium as medium composition (record film composition), a reflecting layer 15nm or less is used.

[0015] It is necessary to form organic or inorganic the protective layer or glue line which does not contain S element substantially on this Ag alloy reflecting layer in this invention. an AgCu alloy -- above -- 80-degree-C85% relative humidity atmosphere -- although sufficient endurance was shown under the following oxidizing atmospheres, in the atmosphere (H2S gas atmosphere etc.) containing S element, melanism was carried out easily It is necessary to form a protective layer or a glue line organic with the purpose which prevents this, or inorganic. As an organic protective layer, ultraviolet-rays hardening type acrylic resin etc. is used.

[0016] 0. When sticking two media of 6mm thickness substrate and considering as a double-sided medium, a pressure sensitive adhesive sheet, hot melt adhesive, and ultraviolet-rays hardening type adhesives are used. As a protective layer of the inorganic thin film which does not contain S element, nitrides, such as SiN and GeN, are desirable. Although ZnS-SiO2 film currently used abundantly at the phase-change type optical recording medium must not be formed on the reflecting layer of this AgCu system, it is possible for forming the reflecting layer of an AgCu alloy on ZnS-SiO2 film conversely.

[0017] Although a well-known vacuum deposition method, the sputtering method, the ion beam sputtering method, CVD, etc. can be considered as the formation method of the aforementioned metallic reflective layer, the sputtering method is desirable in respect of an adhesive property with a ground layer, the controllability of alloy composition, a composition distribution, etc. Moreover, film production conditions, such as the membranous rate of sedimentation and spatter gas pressure, are

suitably chosen in consideration of productivity and membrane stress.
[0018] As for a record layer in case the optical information media of this invention is a phase-change type optical recording medium, chalcogen alloys, such as GeSbTe and AgInSbTe, are used. Especially, this invention is also preferably used from germanium2Sb2Te5 (about 22.2:22.2:germanium:Sb:Te=55.6 atom %) thin film of abbreviation 2:2:5 having [a composition ratio] a repeatedly high over-writing performance, and high-speed elimination being possible.
[0019] As a dielectric layer used for a phase-change type optical recording medium, it is required to do so effects, such as adiabatic efficiency and the optical interference effect, for the purpose, and it is desirable to have the above degree of hardness and high refractive index to some extent. Moreover, a transparent thing is required for the laser beam to be used, and metaled oxide, nitride, sulfide, carbide, fluorides, or these complex can be applied a passage well-known as a transparent dielectric layer. Although silicon oxide, titanium oxide, indium oxide, tantalum oxide, aluminum-oxide, CHITSU-ized silicon, CHITSU-ized germanium, CHITSU-ized tantalum, CHITSU-ized aluminum, CHITSU-ized titanium, zinc sulfide, and magnesium fluoride, aluminum fluoride, silicon carbide, and these composites are specifically mentioned, not being limited to this cannot be overemphasized. Although an optimum value cannot change with medium composition and refractive indexes and the thickness of these transparent dielectric layers cannot be decided uniquely, 10nm - about 150nm is usually used suitably. These transparent ****** are formed by the method more nearly same than the continuity of production as the film production method of a metallic reflective layer.
[0020] As a substrate, although glass, acrylic resin, polycarbonate resin, an epoxy resin, polyolefin resin, those conversion articles, etc. are used suitably, polycarbonate resin is desirable in respect of a mechanical strength, a price, weatherability, thermal resistance, and moisture permeability. The about 120mm disk made from a polycarbonate is preferably used from the diameter of 60mm by the thickness of 0.6 to about 2.0mm by which the substrate used for a phase-change type optical recording medium is produced with injection molding.
[0021] The composition of the phase-change type optical recording medium mainly stated above is the structure of a substrate / a lower dielectric layer / record layer / up dielectric layer / reflecting layer (AgCu alloy) / organic one, an inorganic protective layer, or a glue line. On the other hand, a film surface incidence type phase-change type optical recording medium has at order the basic composition which consists of a reflecting layer / lower dielectric layer / a record layer / an up dielectric layer from a substrate side to one side or both sides of a plastic plate, and record reproduction is carried out from a thin film layered product side, without letting a substrate pass. A glue line and the thermal break for preventing the bad influence of heat in a plastic plate with a substrate low [heat-resistant temperature] may be between a substrate and a reflecting layer. the metallic reflective layer of this invention is more preferably adapted from the outstanding properties, such as a high reflection factor, thermal conductivity, and endurance, being required also of a reflecting layer, since the storage capacity which boiled markedly this film surface incidence type of phase-change type optical recording medium, and was excellent is expected By this film surface incidence type of phase-change type optical recording medium, the protective layer on an AgCu alloy reflecting layer turns into a layer to which the above-mentioned lower dielectric layer is equivalent. Therefore, this lower dielectric layer must not contain S element more than impurity level (substantially). This lower dielectric layer has the aforementioned desirable CHITSU ghost.
[0022] The metallic reflective layer of the AgCu alloy of this invention can be used by all the optical information medias (except for a magneto-optic-recording medium) that have not only a phase-change type optical recording medium but a metallic reflective layer. The organic coloring matter of optical-absorption nature, such as a cyanine dye, can be applied on a polycarbonate substrate, a metallic-reflection film can be formed on this coloring matter film, and it can be adapted also for the metallic reflective layer of the CD-R disk which applies a protective layer on this metallic-reflection film further, and is produced, or a DVD-R disk. Furthermore, it can use also for the reflecting layer of disks only for reproduction, such as CD. An AgCu alloy is there being an equivalent performance from a reflection factor being high, even if thin, and carrying out the reuse of the used raw material (target), although

material's is more expensive than aluminum alloy, and material cost per medium can also be made cheaper than aluminum alloy film.

[0023]

[Examples 1-5, the examples 1 and 2 of comparison] 1. The phase-change type optical recording medium (examples 1-5) which has the composition which consists of a 95nm ZnS-SiO2 lower dielectric layer, a 20nm GeSbTe record layer, a 16nm ZnS-SiO2 up dielectric layer, a 150nm AgCuTi reflecting layer, and an ultraviolet-rays hardening type organic resin protective layer was produced from the substrate side for 2mm thickness and 120mm diameter at order on one side of the plastic plate for optical disks made from a polycarbonate which has a pin center,large hole with a bore of 15mm. Examples 1-5 are the media which changed Ti content of an AgCuTi reflective film into Table 1 like a publication. Although the medium which used only the reflecting layer as Ag film although the medium of the example 1 of comparison was this composition, and the medium of the example 2 of comparison are these composition, they are a medium which used only the reflecting layer as the AlTi film. The spiral slot for continuation servoes (groove) is formed in the substrate by injection molding at the range which is the radius of 24mm - 58mm. A channel depth is 80nm, a track pitch is 1.20 micrometers, and both groove width of face and a land width are about 0.60-micrometer width of face.

[0024] The used sputtering system is RF magnetron-sputtering equipment (SPF-430made from Anelva H type) which converted the substrate electrode-holder section so that an optical disk substrate could be attached. This equipment can install three targets in one vacuum tub, and can form three kinds of films continuously. The used targets are the diameter of 101mm, and size with a thickness of 5mm, and are ZnS-SiO2 target which carried out mixed sintering of ZnS and SiO2 at 80:20-mol % of a rate, the GeSbTe alloy target of germanium:Sb:Te= about 2:2:5 atomic ratios, an AgCu (Cu:10 atom %) alloy target, and an AlTi (Ti:2.0 atom %) alloy target. When producing an AgCuTi film, the spatter of the Ti metal chip of 1mm thickness and 5mm angle was arranged and carried out on the AgCu target. The number of Ti chip and the arrangement on a target were adjusted so that it might become Ti content given in Table 1. Distance of a substrate was set to about 120mm from the target, and spatter film production was carried out by making the position distant from the target center about 100mm into the center of rotation, rotating a substrate by 20rpm (rotation).

[0025] The substrate has been arranged in the vacuum tub of this equipment, it exhausted until it was set to 8x10 to 5 Pa, next, Ar gas was introduced by flow rate 75SCCM in the vacuum tub, and the orifice on a main valve was adjusted so that it might become the pressure of 0.8Pa. As for injection power, the RF power of 500Watt(s) and the spatter of a GeSbTe target used the direct current power of 50Watt(s), as for the time of a ZnS-SiO2 sintered-compact spatter. The direct current power of 400Watt(s) was used at the time of the direct current power of 200Watt(s), and an AlTi target spatter at the time of an AgCu target spatter. For 23.3nm/min. and the AlTi film, 10.2nm/min., the AgCu film, and the AgCuTi film were [ZnS-SiO2 film / 17.3nm/min. and the GeSbTe film of the membranous rate of sedimentation] 20.5nm/min., respectively. Compared with aluminum alloy films, such as an AlTi film by which the rate of sedimentation of the AgCuTi film of this invention is used abundantly now, the rate of sedimentation of power was 1.7 times in the half. When the same power compared, it became the 3.4 times as many rate of sedimentation as this, and it became clear that productivity is very good.

[0026] Furthermore, on the AlCr reflecting layer, applied the phenol novolak epoxy acrylate resin which does not contain ultraviolet-rays hardening type S (sulfur element) by the spin coater, it was made to harden by UV irradiation, about 11-micrometer organic protective layer was prepared, and it considered as the phase-change type optical recording medium.

[0027] The initialization equipment used for initialization (annealing crystallization) is bulk eraser equipment Made from SHIBASOKU (LK101A type). However, laser beam intensity leaned the beam major axis 30 degrees from the disk radial, attached the about 1 maximum watt, wavelength =810nm, NA(objective lens numerical aperture) =0.34, and the spot-size =125micrometer(major-axis length) x1.27micrometer (minor-axis length) thing, and used the used optical head in the disk face of a board. initialization -- linear velocity -- sending [it was fixed 5 m/sec, and] an optical head by the feed rate of 86 micrometers / rotation (speed at which 86 micrometers of optical heads progress to radial at the time

of disk 1 rotation) rotating a disk, the laser power was made into 65% of maximum (namely, about 650mW), and was performed

[0028] Electrical property evaluation of a medium was performed using the Pulstec Industrial DDU-1000 type electrical property evaluation equipment which has the wavelength of 780nm, and the optical head of numerical-aperture NA=0.55 of an objective lens. a place with a rotational-speed 2030rpm [of a disk], and a radius of 26mm -- the write-in frequency of 4MHz, and the single frequency of 62ns of pulse width -- bias power -- record peak power was recorded as adjustable as fixed 4.5 mWatt, and CNR (signal noise ratio) was measured for the signal reproduced by reproduction power 1mWatt by the spectrum analyzer In the standup curve of CNR when enlarging record peak power in order, record peak power when being set to CNR=30dB was made into the evaluation value of record sensitivity. When record sensitivity is too (record is made by too small power) high, the repeat endurance of over-writing becomes bad, if sensitivity is low, excessive power will be required, and the burden of a drive becomes large. Record sensitivity has about 8-12 desirable mWatts. In addition, the value of CNR has the good larger one. An evaluation result is shown in Table 1.

[0029] From the above example, it became clear by the reflective film of only Ag that CNR is low with that record sensitivity is too small and the AlTi reflective film. Furthermore, although about thirty pinholes generated these samples only for the example 1 of comparison when the acceleration deterioration test of 1000 hours was performed on the conditions of the temperature of 80 degrees C, and 85% of humidity, with other samples, change was not seen at all.

[0030] Furthermore, although the medium of an AlTi reflecting layer showed the same performance as the above when the sample made the same up to the place which forms a reflecting layer by the spatter was produced again, and 20nm spatter formation of the ZnS-SiO2 film was carried out on this reflecting layer this time (without it applies an organic protective layer) Surface discoloration was already accepted immediately after the ZnS-SiO2 spatter, and the medium of other Ag reflecting layers and an AgCuTi reflecting layer was presumed that the silver sulfide was generated. And CNR also deteriorated to about 46dB. Furthermore, when spatter formation of not ZnS-SiO2 but the GeN (CHITSU-ized germanium) film was carried out on this reflecting layer, it was all samples and was what any change is not seen, either but can also satisfy a property.

[0031]

[Examples 6-8] Furthermore, except having made it the same as examples 1-5, having arranged the chip of Ta on an AgCu target to relation of Ti, and having merely, used the metallic reflective layer as the AgCuTa alloy of Table 2, the phase-change optical disk of the completely same composition was produced, and it evaluated similarly. The result is shown in Table 2.

[0032] The effect as an AgCuTi film that an AgCuTa film was also the same was checked from this example. Furthermore, in this sample (examples 6, 7, and 8) that applied the organic protective layer, when the acceleration deterioration test of 1000 hours was performed on the conditions of the temperature of 80 degrees C, and 85% of humidity, change was seen at all with no samples, but good environmental endurance was shown.

[0033] As shown in the above example, CNR and sensitivity are excellent in a phase-change type optical recording medium with the metallic-reflection film which consists of an Ag alloy containing either [Cu of this invention, and / at least] Ta or Ti, and an optical information media also with high endurance can be obtained by it. it is remarkable and CNR is also well-known, for example, the fall of the optimal record laser power, i.e., the improvement in record sensitivity, is markedly alike, and especially the content of Ta and Ti excels in it the phase-change optical disk which uses an AlTi alloy film as a reflective film in the range more than 1.5 atom % Especially the content of Ta and Ti has desirable 1.5 - 10 atom % in respect of this effect.

[0034]

[Table 1]

サンプルNo.	AgCuTi反射膜のTi含有量または反射膜の種類	CNR最大値（dB）	記録感度の指標となる記録レーザパワー（mWatt）
実施例1	Ti：0．6原子%	50．5	11．8
実施例2	Ti：1．1原子%	51．0	11．4
実施例3	Ti：2．2原子%	51．1	10．1
実施例4	Ti：5．2原子%	50．7	9．8
実施例5	Ti：10．6原子%	50．0	8．9
比較例1	Ag膜	49．3	13．8
比較例2	AlTi膜 Ti：2．0原子%	47	6．7

[0035]
[Table 2]

サンプルNo.	AgCuTa反射膜のTa含有量	CNR最大値（dB）	記録感度の指標となる記録レーザパワー（mWatt）
実施例6	Ta：0．7原子%	50．3	10．8
実施例7	Ta：1．2原子%	51．2	10．3
実施例8	Ta：6．1原子%	51．0	8．7

[0036]
[Effect of the Invention] As mentioned above, according to the optical information media of this invention, by adopting an AgCu alloy, an AgCuTi alloy, or an AgCuTa alloy as a reflecting layer, it was cheap, and was powerful and it became possible to manufacture the medium excellent in the resistance to environment with sufficient productivity.

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PRIOR ART

[Description of the Prior Art] Various optical information medias (optical disk) are used. As a type only for reproduction, CD (compact disk) and a CD-ROM disk are famous, there is a CD-R disk as a type which can be written in only at once, and there are a magneto-optic-recording disk and a phase-change record disk as a record / eliminable type. As a phase-change disk, the CD-RW disk, PD disk, and the DVD-RAM disk are marketed. It is the most important medium as a mass animation record medium for which a phase-change type optical recording medium attracts attention as mass rewriting types, such as DVD-RW, especially in recent years and which replaces future videotape.

[0003] The phase-change type optical recording medium uses for informational record and elimination the reversible structural change (phase change) between the amorphous state of the record layer in which induction is carried out by the difference in the heat history of the temperature up and cooling by optical irradiation (laser beam irradiation), and a crystallized state. Namely, it eliminates by carrying out heating fusion and quenching a record layer by making it crystallize by recording by making it un-crystallize, and carrying out fixed time maintenance more than crystallization temperature. The temperature of a record layer (typical GeSbTe film) is presumed to become about 600 degrees C at the time of record, and to become about 170 degrees C at the time of elimination. Reproduction of a signal is performed using the reflection factor difference between an amorphous state and a crystallized state. In addition to an informational high-speed throughput, such a phase-change type optical recording medium has large storage capacity. Moreover, the merit made at a low price than it is easier than a magneto-optic-recording drive also has the structure of drives (optical head etc.). By this phase-change type optical recording medium, usually, the crystallized state of record film is made into an informational elimination state, and the amorphous state (amorphous mark) generated by melting of the film by the high laser power and quenching is made into a record state.

[0004] Electronic-intelligence communication society The structure of the typical phase-change disk currently used for present is shown in the technical research report [electronic parts and material] CPM 90-35 and pp 43-48 "the quenching tectofacies change light information media using ZnS-SiO2 dielectric" (July 27, 1990). the structure -- a polycarbonate substrate (it is usually the thickness of 0.6mm or 1.2mm) / a lower dielectric layer (ZnS-SiO2 film) / record layer (GeSbTe film) / up dielectric layer (ZnS-SiO2 film) / reflecting layer (aluminum alloy) / glue line -- it comes out

[0005] Moreover, by the film surface incidence type medium by which research was started, the usual idea makes reverse built-up sequence of the thin film from a substrate to the usual medium of marketing of these present. That is, it inquires with the composition of a substrate / reflective film / lower dielectric / record film / up dielectric. The same structure as a hard disk is proposed according to the need that the optical head (pickup) used makes an objective lens approach a medium side. That is, use of the surfacing head which carried the objective lens in the slider is considered.

[0006] As for the record layer of a phase-change type optical recording medium, chalcogen alloys, such as GeSbTe and AgInSbTe, are used so that the aforementioned reference may see. The film of ZnS systems, such as ZnS-SiO2, is used for a dielectric film. As for the reflecting layer, aluminum alloy film, Au film, Ag film, etc. are used. With aluminum alloy, the AlTi film and AlCr film containing several%

of Ti or Cr are used abundantly. By the media (CD-R disk etc.) which use an organic coloring matter as a record layer, Au film and Ag film are used as a reflecting layer. Generally in CD only for reproduction (compact disk), aluminum film is used.

[Translation done.]

* NOTICES *

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EFFECT OF THE INVENTION

[Effect of the Invention] As mentioned above, according to the optical information media of this invention, by adopting an AgCu alloy, an AgCuTi alloy, or an AgCuTa alloy as a reflecting layer, it was cheap, and was powerful and it became possible to manufacture the medium excellent in the resistance to environment with sufficient productivity.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] aluminum alloy film with which the above is used, Au film, and Ag film have the following technical problems. Although aluminum alloy film is produced by the spatter using the target which consists of this alloy, since the melting point must build this alloy target with the alloy of two kinds of greatly different metals, it is not easy to manufacture, and according to the spatter yield of aluminum being bad, the film rate of sedimentation of sputtering is slow, and it has a fault, like (the reflection factor of a film simple substance) has a reflection factor comparatively as low as 80 - 85%. Although Ag film has about 100% of reflection factor, it has the fault that a corrosion resistance is not good. Although Au film is stable, it is very expensive. That is, the present condition is that search of the reflecting layer which carries out simultaneous satisfaction of all, such as a performance, a price, and production speed, is continued.
[0008] This invention persons proposed the reflecting layer of an AgCuTi alloy and an AgCuTa alloy before. Although the alloy film in that case was applied to the magneto-optic-recording medium and achieved fixed success, it has a technical-problem **** case in the application of those other than a magneto-optic-recording medium, and sufficient result was not obtained. Especially, by the phase-change type optical recording medium, the technical problem that Ag would sulfurate and a reflection factor would fall on the reflecting layer of Ag system alloy if spatter film production of this dielectric film is carried out occurred from using ZnS-SiO2 film as a dielectric layer.
[0009] It was made in view of this present condition, and a reflection factor is high and this invention excels [reflection factor] in corrosion resistance, and it is specifying the good reflecting layer of productivity, and the protective layer on it, and it aims at offering a highly efficient and cheap optical information media, especially a phase-change type optical recording medium.

[Translation done.]

* NOTICES *

MEANS

[Means for Solving the Problem] This invention persons found out that the optical information media which formed the metallic reflective layer with the AgCu alloy, and was cheap with high performance by preparing organic or inorganic the protective layer or glue line which does not contain S (sulfur) on this metallic reflective layer, was excellent in productivity, and was further excellent in stability with the passage of time was obtained, as a result of considering wholeheartedly improvement of the metallic reflective layer which carries out simultaneous satisfaction of all, such as a performance, a price, and production speed, like the above.

[0011] That is, in the optical information media except the magneto-optic-recording medium by which this invention has a metallic reflective layer, this metallic reflective layer is the optical information media characterized by forming organic or inorganic the protective layer or glue line which consists of an Ag alloy to carry out, and does not contain S element substantially on this metallic reflective layer 0.5-30 atom % content about Cu (copper) at Ag (silver). Furthermore, this invention is an optical information media which carries out and makes a reflecting layer further Ag alloy of Ta (tantalum) or Ti (titanium) which does 0.5-12 atom % content of a kind at least 0.5-30 atom % content about Cu at Ag. Moreover, the metallic reflective layer of this invention is preferably applied to a phase-change type optical recording medium.

[0012]

[Embodiments of the Invention] Although this invention persons paid their attention to Ag film of a high reflection factor for the purpose of the improvement in a regenerative-signal noise ratio (C/N), Ag is a corrosion resistance bad material and they are not practical only by Ag film. Then, when addition of other metals was considered as this improvement, the AgCu alloy film which did 0.5-30 atom % addition of Cu formed on slide glass was a high reflection factor, even if it left it for 72 hours or more under the 80-degree-C85% relative humidity atmosphere which is the standard acceleration degradation test condition of an optical information media, a reflection factor did not fall, but a certain thing also made endurance clear. In addition, even if there were few contents of Cu than 0.5 atom %, the reflection factor fell to 90 or less percent of initial value within at most 24 hours from 30 atom %. The AgCu alloy film was as above-mentioned a quantity reflection factor (for example, with an Ag85Cu15 (subscript is atomic % composition) alloy film, it is 98% of reflection factor at the wavelength of 780nm), and since endurance was not bad, either, it made it clear that it is suitable for the optical information media only for reproduction. However, this AgCu film had high thermal conductivity, therefore it became clear further that record sensitivity falls by the phase-change type optical recording medium which makes this a reflective film.

[0013] Further, paying attention to improvement of this point, wholeheartedly, this invention persons found out the thing of Ta or Ti which record sensitivity and corrosion resistance improve greatly to addition of the 3rd element at the AgCu film as a result of research, when 0.5-12 atom % addition of a kind was done at least. In addition, when there are few contents of Ta and Ti than this range, there is no effect of improvement in record sensitivity, and if it increases conversely, reflection will fall and C/N will become bad. Furthermore, 1.5 - 10 atom % is more desirable at the point that the content of Ta and

Ti has the large improvement effect in sensitivity, and the effect of the improvement in C/N is not checked by the phase-change type optical recording medium. In addition, in order to improve stability with the passage of time further, you may carry out little addition of other elements, such as Cr, Nb, and Re.

[0014] The thickness of this metallic reflective layer is used preferably 3-200nm. When considering absorption coefficient amendment composition which makes the rate of an optical absorption in case a record layer is a crystallized state larger than the rate of an optical absorption at the time of an amorphous state by the phase-change type optical recording medium as medium composition (record film composition), a reflecting layer 15nm or less is used.

[0015] It is necessary to form organic or inorganic the protective layer or glue line which does not contain S element substantially on this Ag alloy reflecting layer in this invention. an AgCu alloy -- above -- 80-degree-C85% relative humidity atmosphere -- although sufficient endurance was shown under the following oxidizing atmospheres, in the atmosphere (H2S gas atmosphere etc.) containing S element, melanism was carried out easily It is necessary to form a protective layer or a glue line organic with the purpose which prevents this, or inorganic. As an organic protective layer, ultraviolet-rays hardening type acrylic resin etc. is used.

[0016] 0. When sticking two media of 6mm thickness substrate and considering as a double-sided medium, a pressure sensitive adhesive sheet, hot melt adhesive, and ultraviolet-rays hardening type adhesives are used. As a protective layer of the inorganic thin film which does not contain S element, nitrides, such as SiN and GeN, are desirable. Although ZnS-SiO2 film currently used abundantly at the phase-change type optical recording medium must not be formed on the reflecting layer of this AgCu system, it is possible for forming the reflecting layer of an AgCu alloy on ZnS-SiO2 film conversely.

[0017] Although a well-known vacuum deposition method, the sputtering method, the ion beam sputtering method, CVD, etc. can be considered as the formation method of the aforementioned metallic reflective layer, the sputtering method is desirable in respect of an adhesive property with a ground layer, the controllability of alloy composition, a composition distribution, etc. Moreover, film production conditions, such as the membranous rate of sedimentation and spatter gas pressure, are suitably chosen in consideration of productivity and membrane stress.

[0018] As for a record layer in case the optical information media of this invention is a phase-change type optical recording medium, chalcogen alloys, such as GeSbTe and AgInSbTe, are used. Especially, this invention is also preferably used from germanium2Sb2Te5 (about 22.2:22.2:germanium:Sb:Te=55.6 atom %) thin film of abbreviation 2:2:5 having [a composition ratio] a repeatedly high over-writing performance, and high-speed elimination being possible.

[0019] As a dielectric layer used for a phase-change type optical recording medium, it is required to do so effects, such as adiabatic efficiency and the optical interference effect, for the purpose, and it is desirable to have the above degree of hardness and high refractive index to some extent. Moreover, a transparent thing is required for the laser beam to be used, and metaled oxide, nitride, sulfide, carbide, fluorides, or these complex can be applied a passage well-known as a transparent dielectric layer. Although silicon oxide, titanium oxide, indium oxide, tantalum oxide, aluminum-oxide, CHITSU-ized silicon, CHITSU-ized germanium, CHITSU-ized tantalum, CHITSU-ized aluminum, CHITSU-ized titanium, zinc sulfide, and magnesium fluoride, aluminum fluoride, silicon carbide, and these composites are specifically mentioned, not being limited to this cannot be overemphasized. Although an optimum value cannot change with medium composition and refractive indexes and the thickness of these transparent dielectric layers cannot be decided uniquely, 10nm - about 150nm is usually used suitably. These transparent ****** are formed by the method more nearly same than the continuity of production as the film production method of a metallic reflective layer.

[0020] As a substrate, although glass, acrylic resin, polycarbonate resin, an epoxy resin, polyolefin resin, those conversion articles, etc. are used suitably, polycarbonate resin is desirable in respect of a mechanical strength, a price, weatherability, thermal resistance, and moisture permeability. The about 120mm disk made from a polycarbonate is preferably used from the diameter of 60mm by the thickness of 0.6 to about 2.0mm by which the substrate used for a phase-change type optical recording medium is

produced with injection molding.
[0021] The composition of the phase-change type optical recording medium mainly stated above is the structure of a substrate / a lower dielectric layer / record layer / up dielectric layer / reflecting layer (AgCu alloy) / organic one, an inorganic protective layer, or a glue line. On the other hand, a film surface incidence type phase-change type optical recording medium has at order the basic composition which consists of a reflecting layer / lower dielectric layer / a record layer / an up dielectric layer from a substrate side to one side or both sides of a plastic plate, and record reproduction is carried out from a thin film layered product side, without letting a substrate pass. A glue line and the thermal break for preventing the bad influence of heat in a plastic plate with a substrate low [heat-resistant temperature] may be between a substrate and a reflecting layer. the metallic reflective layer of this invention is more preferably adapted from the outstanding properties, such as a high reflection factor, thermal conductivity, and endurance, being required also of a reflecting layer, since the storage capacity which boiled markedly this film surface incidence type of phase-change type optical recording medium, and was excellent is expected By this film surface incidence type of phase-change type optical recording medium, the protective layer on an AgCu alloy reflecting layer turns into a layer to which the above-mentioned lower dielectric layer is equivalent. Therefore, this lower dielectric layer must not contain S element more than impurity level (substantially). This lower dielectric layer has the aforementioned desirable CHITSU ghost.
[0022] The metallic reflective layer of the AgCu alloy of this invention can be used by all the optical information medias (except for a magneto-optic-recording medium) that have not only a phase-change type optical recording medium but a metallic reflective layer. The organic coloring matter of optical-absorption nature, such as a cyanine dye, can be applied on a polycarbonate substrate, a metallic-reflection film can be formed on this coloring matter film, and it can be adapted also for the metallic reflective layer of the CD-R disk which applies a protective layer on this metallic-reflection film further, and is produced, or a DVD-R disk. Furthermore, it can use also for the reflecting layer of disks only for reproduction, such as CD. An AgCu alloy is there being an equivalent performance from a reflection factor being high, even if thin, and carrying out the reuse of the used raw material (target), although material's is more expensive than aluminum alloy, and material cost per medium can also be made cheaper than aluminum alloy film.
[0023]
[Examples 1-5, the examples 1 and 2 of comparison] 1. The phase-change type optical recording medium (examples 1-5) which has the composition which consists of a 95nm ZnS-SiO2 lower dielectric layer, a 20nm GeSbTe record layer, a 16nm ZnS-SiO2 up dielectric layer, a 150nm AgCuTi reflecting layer, and an ultraviolet-rays hardening type organic resin protective layer was produced from the substrate side for 2mm thickness and 120mm diameter at order on one side of the plastic plate for optical disks made from a polycarbonate which has a pin center,large hole with a bore of 15mm. Examples 1-5 are the media which changed Ti content of an AgCuTi reflective film into Table 1 like a publication. Although the medium which used only the reflecting layer as Ag film although the medium of the example 1 of comparison was this composition, and the medium of the example 2 of comparison are these composition, they are a medium which used only the reflecting layer as the AlTi film. The spiral slot for continuation servoes (groove) is formed in the substrate by injection molding at the range which is the radius of 24mm - 58mm. A channel depth is 80nm, a track pitch is 1.20 micrometers, and both groove width of face and a land width are about 0.60-micrometer width of face.
[0024] The used sputtering system is RF magnetron-sputtering equipment (SPF-430made from Anelva H type) which converted the substrate electrode-holder section so that an optical disk substrate could be attached. This equipment can install three targets in one vacuum tub, and can form three kinds of films continuously. The used targets are the diameter of 101mm, and size with a thickness of 5mm, and are ZnS-SiO2 target which carried out mixed sintering of ZnS and SiO2 at 80:20-mol % of a rate, the GeSbTe alloy target of germanium:Sb:Te= about 2:2:5 atomic ratios, an AgCu (Cu:10 atom %) alloy target, and an AlTi (Ti:2.0 atom %) alloy target. When producing an AgCuTi film, the spatter of the Ti metal chip of 1mm thickness and 5mm angle was arranged and carried out on the AgCu target. The

number of Ti chip and the arrangement on a target were adjusted so that it might become Ti content given in Table 1. Distance of a substrate was set to about 120mm from the target, and spatter film production was carried out by making the position distant from the target center about 100mm into the center of rotation, rotating a substrate by 20rpm (rotation).

[0025] The substrate has been arranged in the vacuum tub of this equipment, it exhausted until it was set to 8x10 to 5 Pa, next, Ar gas was introduced by flow rate 75SCCM in the vacuum tub, and the orifice on a main valve was adjusted so that it might become the pressure of 0.8Pa. As for injection power, the RF power of 500Watt(s) and the spatter of a GeSbTe target used the direct current power of 50Watt(s), as for the time of a ZnS-SiO2 sintered-compact spatter. The direct current power of 400Watt(s) was used at the time of the direct current power of 200Watt(s), and an AlTi target spatter at the time of an AgCu target spatter. For 23.3nm/min. and the AlTi film, 10.2nm/min., the AgCu film, and the AgCuTi film were [ZnS-SiO2 film / 17.3nm/min. and the GeSbTe film of the membranous rate of sedimentation] 20.5nm/min., respectively. Compared with aluminum alloy films, such as an AlTi film by which the rate of sedimentation of the AgCuTi film of this invention is used abundantly now, the rate of sedimentation of power was 1.7 times in the half. When the same power compared, it became the 3.4 times as many rate of sedimentation as this, and it became clear that productivity is very good.

[0026] Furthermore, on the AlCr reflecting layer, applied the phenol novolak epoxy acrylate resin which does not contain ultraviolet-rays hardening type S (sulfur element) by the spin coater, it was made to harden by UV irradiation, about 11-micrometer organic protective layer was prepared, and it considered as the phase-change type optical recording medium.

[0027] The initialization equipment used for initialization (annealing crystallization) is bulk eraser equipment Made from SHIBASOKU (LK101A type). However, laser beam intensity leaned the beam major axis 30 degrees from the disk radial, attached the about 1 maximum watt, wavelength =810nm, NA(objective lens numerical aperture) =0.34, and the spot-size =125micrometer(major-axis length) x1.27micrometer (minor-axis length) thing, and used the used optical head in the disk face of a board. initialization -- linear velocity -- sending [it was fixed 5 m/sec, and] an optical head by the feed rate of 86 micrometers / rotation (speed at which 86 micrometers of optical heads progress to radial at the time of disk 1 rotation) rotating a disk, the laser power was made into 65% of maximum (namely, about 650mW), and was performed

[0028] Electrical property evaluation of a medium was performed using the Pulstec Industrial DDU-1000 type electrical property evaluation equipment which has the wavelength of 780nm, and the optical head of numerical-aperture NA=0.55 of an objective lens. a place with a rotational-speed 2030rpm [of a disk], and a radius of 26mm -- the write-in frequency of 4MHz, and the single frequency of 62ns of pulse width -- bias power -- record peak power was recorded as adjustable as fixed 4.5 mWatt, and CNR (signal noise ratio) was measured for the signal reproduced by reproduction power 1mWatt by the spectrum analyzer In the standup curve of CNR when enlarging record peak power in order, record peak power when being set to CNR=30dB was made into the evaluation value of record sensitivity. When record sensitivity is too (record is made by too small power) high, the repeat endurance of over-writing becomes bad, if sensitivity is low, excessive power will be required, and the burden of a drive becomes large. Record sensitivity has about 8-12 desirable mWatts. In addition, the value of CNR has the good larger one. An evaluation result is shown in Table 1.

[0029] From the above example, it became clear by the reflective film of only Ag that CNR is low with that record sensitivity is too small and the AlTi reflective film. Furthermore, although about thirty pinholes generated these samples only for the example 1 of comparison when the acceleration deterioration test of 1000 hours was performed on the conditions of the temperature of 80 degrees C, and 85% of humidity, with other samples, change was not seen at all.

[0030] Furthermore, although the medium of an AlTi reflecting layer showed the same performance as the above when the sample made the same up to the place which forms a reflecting layer by the spatter was produced again, and 20nm spatter formation of the ZnS-SiO2 film was carried out on this reflecting layer this time (without it applies an organic protective layer) Surface discoloration was already accepted immediately after the ZnS-SiO2 spatter, and the medium of other Ag reflecting layers and an

AgCuTi reflecting layer was presumed that the silver sulfide was generated. And CNR also deteriorated to about 46dB. Furthermore, when spatter formation of not ZnS-SiO2 but the GeN (CHITSU-ized germanium) film was carried out on this reflecting layer, it was all samples and was what any change is not seen, either but can also satisfy a property.

[0031]

[Examples 6-8] Furthermore, except having made it the same as examples 1-5, having arranged the chip of Ta on an AgCu target to relation of Ti, and having merely, used the metallic reflective layer as the AgCuTa alloy of Table 2, the phase-change optical disk of the completely same composition was produced, and it evaluated similarly. The result is shown in Table 2.

[0032] The effect as an AgCuTi film that an AgCuTa film was also the same was checked from this example. Furthermore, in this sample (examples 6, 7, and 8) that applied the organic protective layer, when the acceleration deterioration test of 1000 hours was performed on the conditions of the temperature of 80 degrees C, and 85% of humidity, change was seen at all with no samples, but good environmental endurance was shown.

[0033] As shown in the above example, CNR and sensitivity are excellent in a phase-change type optical recording medium with the metallic-reflection film which consists of an Ag alloy containing either [Cu of this invention, and / at least] Ta or Ti, and an optical information media also with high endurance can be obtained by it. it is remarkable and CNR is also well-known, for example, the fall of the optimal record laser power, i.e., the improvement in record sensitivity, is markedly alike, and especially the content of Ta and Ti excels in it the phase-change optical disk which uses an AlTi alloy film as a reflective film in the range more than 1.5 atom % Especially the content of Ta and Ti has desirable 1.5 - 10 atom % in respect of this effect.

[0034]

[Table 1]

サンプルNo.	AgCuTi反射膜のTi含有量または反射膜の種類	CNR最大値（dB）	記録感度の指標となる記録レーザパワー（mWatt）
実施例1	Ti：0．6原子%	50．5	11．8
実施例2	Ti：1．1原子%	51．0	11．4
実施例3	Ti：2．2原子%	51．1	10．1
実施例4	Ti：5．2原子%	50．7	9．8
実施例5	Ti：10．6原子%	50．0	8．9
比較例1	Ag膜	49．3	13．8
比較例2	AlTi膜 Ti：2．0原子%	47	6．7

[0035]

[Table 2]

サンプルNo.	AgCuTa反射膜のTa含有量	CNR最大値（dB）	記録感度の指標となる記録レーザパワー（mWatt）
実施例6	Ta：0．7原子%	50．3	10．8
実施例7	Ta：1．2原子%	51．2	10．3
実施例8	Ta：6．1原子%	51．0	8．7

[Translation done.]